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Synthesis, crystal structure and characterization of the heterometallic tetranuclear butterfly cluster $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$

Aapo U. Härkönen ^a, Markku Ahlgrén ^a, Tapani A. Pakkanen ^{a,*}, Jouni Pursiainen ^b

^a Department of Chemistry, University of Joensuu, PO Box 111, FIN-80101 Joensuu, Finland

^b Department of Chemistry, University of Oulu, Linnanmaa, PO Box 333, FIN-90571 Oulu, Finland

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Abstract

A new iridium–ruthenium mixed-metal cluster $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$ has been synthesized and its structure has been determined by single-crystal X-ray diffraction. $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$ shows a butterfly arrangement of metal atoms; with three terminal carbonyls on each metal atom and with the hydride ligands at Ru–Ru edges.

Keywords: Ruthenium; Iridium; Cluster; Carbonyl; Crystal structure; Heterometallic cluster

1. Introduction

Although there have been a number of studies of mixed-metal clusters (see for example Ref. [1]), only a few compounds containing a ruthenium and iridium mixed-metal framework are known. Structural information is available for an anionic cluster, $[\text{RuIr}_3(\text{CO})_{12}]^-$ [2] and for a phosphine complex of the Ru_3Ir frame, $[\text{Ru}_3\text{IrH}_2(\text{CO})_8(\text{PPh}_3)(\mu\text{-PPh}_2)(\text{PPhC}_6\text{H}_4)]$ [3].

Butterfly structures are found in many tetranuclear clusters with a wide variety of bridging ligands. Among the more extensively studied compounds are those containing a main-group atom such as carbon [4], nitrogen [5], oxygen [6], sulfur [7], and chlorine [8] in the bridging position. Typically, tetranuclear Fe [9] and Ru [10] clusters are known to form butterfly structures including mixed-metal butterfly compounds such as $[\text{Ru}_3\text{CoH}(\text{CO})_{12}(\text{SMe}_2)]$ [7], $[\text{Ru}_3\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\text{H}_4(\text{CO})_9]$ [11] and $[\text{Ru}_3\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\text{H}(\text{CO})_{10}\text{BH}_2]$ [11]. The 64-electron cluster $[\text{Ru}_3\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\text{H}(\text{CO})_{10}\text{BH}_2]$ has been characterized structurally and spectroscopically. Its cluster core can be described either as an open-butterfly or a spiked triangle which is supported by a μ_4 -boron atom. Additionally, a neutral 60-electron butterfly cluster $[\text{Ru}_3\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\text{H}_4(\text{CO})_9]$ has been

characterized spectroscopically. We report here the synthesis and X-ray crystal structure of a new chloride-bridged butterfly cluster containing ruthenium and iridium.

2. Results and discussion

2.1. Synthesis and structure of $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$

$\text{Na}[\text{Ru}_3\text{H}(\text{CO})_{11}]$ and $[\text{Ir}(\text{CO})_3\text{Cl}]_n$ were allowed to react in tetrahydrofuran (thf) for 2 h yielding 22% of the title compound.

The crystal structure of $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$ possesses a butterfly arrangement of four metal atoms with the chloride bridging the two ruthenium ‘wings’. The iridium atom is located on the hinge bond of the butterfly structure. The structure is presented in Fig. 1, the atomic coordinates are shown in Table 1, bond distances in Table 2, and selected bond angles in Table 3.

The structure of $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$ has a crystallographic mirror plane passing through the chloride ligand, the Ru(1) and Ir atoms. The Ru(2)–Cl–Ru(2a) bridge angle (94.5°) is more obtuse-angled than corresponding angles in other halogen-bridged compounds. For example, the metal–halogen–metal bond angles are 88.3° for $[\text{PPN}][\text{Ru}_4(\text{CO})_{13}\text{Cl}]$ [8] and 87.9° for $[\text{Os}_4\text{H}_3(\text{CO})_{12}\text{I}]$ [12]. In the structure of $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$ the observed widening of the metal–halo-

* Corresponding author.

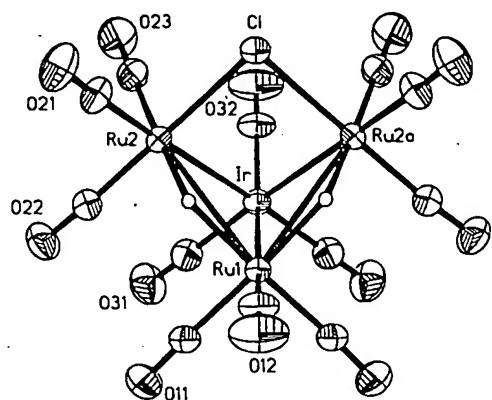


Fig. 1. Thermal ellipsoid labeling diagram for $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$. The thermal ellipsoids are drawn at the 40% probability level.

gen-metal bond angles may be a consequence of hydrogen-bridged bonds at the wing edges.

The cluster structure is comparable with butterfly structures of $[\text{Ru}_4\text{H}_2(\text{CO})_{12}(\text{SMe}_2)]$ [7] and mixed-metal $[\text{Ru}_3\text{CoH}(\text{CO})_{12}(\text{SMe}_2)]$ [7]. The structure of the $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$ is a wing-tip-bridged butterfly cluster with dihedral angle of 89.3° . Corresponding values for the dihedral angles for Ru_4 and Ru_3Co clusters are 94.8° and 96.1° respectively. Although the dihedral angle of $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$ is smaller than the corresponding similar angles of Ru_4 and Ru_3Co clusters, these values are typical for wing-tip-bridged 62-electron butterfly clusters [13]. Each metal atom bears three terminal carbonyl ligands. The wing Ru–Ir bond distance of $2.789(6)$ Å and the hinge Ru–Ru bond distance

Table 2
Selected bond lengths (Å) for $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$

| | | | |
|-------------|----------|-------------|----------|
| Ir–Ru(1) | 2.729(1) | Ru(2)–C(23) | 1.905(7) |
| Ir–Ru(2) | 2.789(1) | Ru(1)–H | 1.770(6) |
| Ru(1)–Ru(2) | 2.989(1) | Ru(2)–H | 1.680(6) |
| Cl–Ru(2) | 2.431(1) | O(11)–C(11) | 1.121(8) |
| Ir–C(31) | 1.914(7) | O(12)–C(12) | 1.161(1) |
| Ir–C(32) | 1.877(9) | C(21)–O(21) | 1.096(9) |
| Ru(1)–C(11) | 1.907(7) | C(22)–O(22) | 1.130(8) |
| Ru(1)–C(12) | 1.924(9) | C(23)–O(23) | 1.136(8) |
| Ru(2)–C(21) | 1.968(7) | O(31)–C(31) | 1.124(9) |
| Ru(2)–C(22) | 1.874(7) | O(32)–C(32) | 1.146(1) |

of $2.729(8)$ Å are nearly equal in $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$, but the wing Ru–Ru bond distances of $2.989(7)$ Å are clearly longer than the remaining bonds, which implies hydrogen-bridged bonds [14]. The wing bond distances of Ru–Ir are clearly shorter than in the Ru_4 ($2.852(3)$ Å) and Ru_3Co ($2.872(2)$ Å) butterfly clusters, but the Ru–Ir hinge bond distance is a little longer than the corresponding bonds in Ru_3Co ($2.651(2)$ Å) cluster but a little shorter than Ru_4 ($2.875(2)$ Å) cluster [7].

After anisotropic refinement ($R = 0.042$), the hydride ligands were found using Fourier difference calculations. The bridging hydride ligands lengthen metal-metal bonds and have a repulsive effect on the carbonyl groups. The hydride-bridged Ru(1)–Ru(2) bond of 2.989 Å is longer than the hinge bond Ir–Ru(1) of 2.759 Å and the wing Ru–Ru bond of 2.789 Å (Table 2). The bond angles Ru(2)/Ru(2a)–Ru(1)–C(12) are $114.5(2)^\circ$, whereas in $[\text{Ru}_4\text{H}_2(\text{CO})_{12}(\text{SMe}_2)]$ and $[\text{Ru}_3\text{CoH}-$

Table 1
Atomic coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$) for $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$

| Atom | x | y | z | U^a |
|-------|-----------|---------|-----------|-------|
| Ir | 3783(1) | 2500 | 1941(1) | 33(1) |
| Ru(1) | 29(1) | 2500 | –80(1) | 30(1) |
| Ru(2) | 1512(1) | 3600(1) | 2874(1) | 33(1) |
| Cl | 1019(3) | 2500 | 4573(3) | 42(1) |
| O(11) | 557(12) | 3811(4) | –2353(8) | 73(2) |
| O(12) | –4346(11) | 2500 | –1850(10) | 73(3) |
| O(21) | –1629(9) | 4521(4) | 3627(8) | 69(2) |
| O(22) | 2169(9) | 4996(3) | 878(7) | 62(2) |
| O(23) | 4873(10) | 4171(4) | 5875(8) | 81(2) |
| O(31) | 5148(11) | 3892(5) | 314(10) | 79(2) |
| O(32) | 6974(12) | 2500 | 5287(11) | 93(4) |
| C(11) | 396(10) | 3334(4) | –1481(7) | 45(1) |
| C(12) | –2703(13) | 2500 | –1154(10) | 44(2) |
| C(21) | –491(11) | 4206(4) | 3353(9) | 48(1) |
| C(22) | 1918(10) | 4458(4) | 1597(8) | 43(1) |
| C(23) | 3625(11) | 3953(5) | 4752(9) | 52(2) |
| C(31) | 4617(10) | 3381(5) | 905(9) | 49(2) |
| C(32) | 5713(14) | 2500 | 4049(12) | 53(2) |
| H | –348(9) | 3246(4) | 1256(7) | 28(2) |

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U tensor.

Table 3
Selected bond angles (deg) for $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$

| | | | |
|--------------------|----------|-------------------|----------|
| C(32)–Ir–C(31) | 100.9(3) | Ru(2a)–Ru(1)–H | 87(2) |
| C(31)–Ir–C(31a) | 96.7(4) | Ru(2a)–Cl–Ru(2) | 94.5(1) |
| C(32)–Ir–Ru(1) | 151.5(3) | O(12)–C(12)–Ru(1) | 177.9(8) |
| C(31)–Ir–Ru(1) | 97.9(2) | O(11)–C(11)–Ru(1) | 177.4(7) |
| C(32)–Ir–Ru(2) | 93.1(2) | O(31)–C(31)–Ir | 178.4(7) |
| C(31)–Ir–Ru(2) | 90.0(2) | O(32)–C(32)–Ir | 175.6(1) |
| C(31a)–Ir–Ru(2) | 163.0(2) | C(22)–Ru(2)–C(23) | 91.0(3) |
| C(11)–Ru(1)–C(11a) | 90.5(4) | C(22)–Ru(2)–C(21) | 93.3(3) |
| C(11)–Ru(1)–C(12) | 93.9(3) | C(23)–Ru(2)–C(21) | 97.6(3) |
| C(11)–Ru(1)–Ir | 93.1(2) | C(22)–Ru(2)–Cl | 179.0(2) |
| C(12)–Ru(1)–Ir | 170.0(2) | C(23)–Ru(2)–Cl | 88.0(2) |
| C(11)–Ru(1)–Ru(2) | 91.7(2) | C(21)–Ru(2)–Cl | 86.5(2) |
| C(11a)–Ru(1)–Ru(2) | 151.3(2) | C(22)–Ru(2)–Ir | 93.1(2) |
| C(12)–Ru(1)–Ru(2) | 114.5(2) | C(23)–Ru(2)–Ir | 91.9(3) |
| C(11)–Ru(1)–H | 92(2) | C(21)–Ru(2)–Ir | 168.4(2) |
| C(11a)–Ru(1)–H | 178(2) | Cl–Ru(2)–Ir | 87.3(1) |
| C(12)–Ru(1)–H | 86(2) | C(22)–Ru(2)–Ru(1) | 91.5(2) |
| Ir–Ru(1)–H | 87(2) | C(23)–Ru(2)–Ru(1) | 148.1(3) |
| Ru(2)–Ru(1)–H | 29(2) | C(21)–Ru(2)–Ru(1) | 113.9(2) |
| C(22)–Ru(2)–H | 91(2) | Cl–Ru(2)–Ru(1) | 89.5(1) |
| C(23)–Ru(2)–H | 177(2) | Cl–Ru(2)–H | 90(2) |
| C(21)–Ru(2)–H | 83(2) | O(22)–C(22)–Ru(2) | 177.2(6) |
| Ir–Ru(2)–H | 87(2) | O(21)–C(21)–Ru(2) | 177.8(7) |
| Ru(1)–Ru(2)–H | 31(2) | O(23)–C(23)–Ru(2) | 179.2(8) |

(CO)₁₂(SMe₂) the corresponding angles for the hydride-bridged metal–metal edge are 109.5(4)° and 132.0(4)° respectively, and the non-bridged metal–metal edge angles are 84.9(4)° and 69.8(4)° respectively. In [Ru₄H₂(CO)₁₂(SMe₂)] one hydrogen-bridged bond is in the hinge position and the other in the wing side, as in [Ru₃CoH(CO)₁₂(SMe₂)].

In CDCl₃ solution, the room-temperature ¹H NMR spectrum of [Ru₃IrH₂(CO)₁₂Cl] exhibits one sharp hydride resonance at δ = 18.7 ppm. It can be assigned to the Ru(μ₂-H)Ru bridging hydrogen atoms which are equivalent.

In future work the goal is to find ways to eliminate the chlorine ligand to give the neutral hydride butterfly cluster compound [Ru₃IrH₃(CO)₁₂] and find synthetic methods to produce new ruthenium and iridium mixed-metal clusters, with either closed or open frames.

3. Experimental section

3.1. General comments

All manipulations except chromatographic separations were carried out under a nitrogen atmosphere and with deoxygenated solvents. [Ir(CO)₃Cl]_n was of commercial origin (Strem). Na[Ru₃H(CO)₁₁] [15] was prepared by published methods.

Infrared spectra were recorded in *n*-hexane on a Nicolet 20SXC FT-IR spectrometer. The ¹H NMR spectra were measured on a Bruker AM-250 spectrometer with CDCl₃ as solvent at 273 K with Me₄Si as reference. Crystals were grown by evaporation of the solvent from a saturated hexane–CH₂Cl₂ solution.

3.2. Synthesis of [Ru₃IrH₂(CO)₁₂Cl]

The compound [Ir(CO)₃Cl]_n (37 mg, 0.118 mmol) was added to a solution of Na[Ru₃H(CO)₁₁] (134 mg, 0.211 mmol) in thf (50 ml). The solution was stirred at room-temperature for 2 h. The reddish-brown solution was filtered and evaporated in vacuo and the residue was extracted by hexane and CH₂Cl₂. Hexane extract showed CO-stretching vibrations characteristic for [Ru₃(CO)₁₂]. Dichloromethane extract was chromatographed with thin layer chromatography. Elution of CH₂Cl₂ extract with a hexane–dichloromethane (5:1) mixture gave a yellow band that showed CO-stretching vibrations characteristic for [Ru₃(CO)₁₂] (27 mg). Further elution with a hexane–dichloromethane (5:1) mixture gave a reddish-brown fraction, which was dried in vacuo and recrystallized from hexane–dichloromethane at 4 °C. Air-stable dark red cubic crystals were formed; yield 23 mg (22%). IR: ν(CO) 2089 w, 2078 s, 2067 s, 2054 vs, 2035 w, 2023 m, 2006 w cm⁻¹. ¹H NMR: –18.7 (s) ppm. A fraction that was not eluted by a

Table 4
Crystallographic data for [Ru₃IrH₂(CO)₁₂Cl]

| | |
|---|--|
| Formula | C ₁₂ H ₂ ClIrO ₁₂ Ru ₃ |
| Formula weight | 869.0 |
| Crystal system | monoclinic |
| Space group | P2 ₁ /m |
| a(Å) | 7.527(1) |
| b(Å) | 16.233(3) |
| c(Å) | 8.693(1) |
| β(deg) | 111.42(1) |
| V(Å ³) | 988.8(3) |
| Z | 2 |
| D _{calc} (g cm ⁻³) | 2.92 |
| Crystal dimensions (mm ³) | 0.4 × 0.4 × 0.5 |
| Radiation | Mo K α |
| Monochromator | graphite |
| 2θ limits (deg) | 5–65 |
| No. of reflections measured | 3921 |
| No. of unique data | 3702 |
| No. of I > 2σ(I) | 3195 |
| μ(Mo K α) (cm ⁻¹) | 95.0 |
| R[I > 2σ(I)] ^a | 0.042 |
| wR(F ²) ^b | 0.109 |
| S (goodness of fit) | 1.093 |

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b weight = $1/[\sigma^2(F_o^2) + (0.0498P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

hexane–dichloromethane (5:1) mixture remained. Attempts to crystallize this fraction failed.

3.3. Crystallographic summary

Pertinent crystal and refinement data are listed in Table 4. Data were collected on a Nicolet R3m diffractometer using Mo K α radiation (λ = 0.71073 Å). Accurate cell parameters were obtained from 25 automatically centered reflections in the range 15 < 2θ < 35°. Intensities were corrected for background, polarization, and Lorentz factors. Empirical absorption corrections were made from ψ-scan data. Transmission factors being $T_{\min} = 0.113$ and $T_{\max} = 0.178$.

The metal atom positions were solved by direct methods using the SHELXTL program package [16]. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least squares refinement and difference electron density syntheses using SHELXL93 [17]. Metal, oxygen, chlorine, and carbon atoms were anisotropically refined in the structure. Hydride ligands were located from a difference Fourier map but not refined.

A complete list of bond lengths and angles and tables of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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